

DRAWINGS ATTACHED.

1,152,577



Date of Application and filing Complete Specification:

16 May, 1966.

No. 21656/66.

Application made in United States of America (No. 456,214) on
17 May, 1965.

(Patent of Addition to No. 994,769 dated 25 March, 1964).

Complete Specification Published: 21 May, 1969.

© Crown Copyright 1969.

Index at Acceptance:—C2 C(3A10B2C, 3A10B5C, 3A10B5G1).

Int. Cl.:—C 07 c 63/14.

COMPLETE SPECIFICATION.

Purification of Aromatic Polycarboxylic Acids.

We, STANDARD OIL COMPANY, a Corporation organised and existing under the laws of the State of Indiana, United States of America, of 910 South Michigan Avenue, Chicago, 60680, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of polycarboxylic aromatic acids, and more particularly concerns the preparation of polycarboxylic aromatic acids having a purity sufficient for direct esterification with diols to produce super polyesters. Though the process of the invention is mainly described herein as applied to the purification of crude terephthalic acid to produce terephthalic acid of fiber-grade quality, it is not limited thereto and it includes the purification of other polycarboxylic aromatic acids such as, for example, trimesic, isophthalic, naphthalene dicarboxylic, trimellitic and mellitic acids.

High molecular weight polyesters of terephthalic acid with various diols find extensive use as synthetic fibers and film. These super polyesters, first described in British Patent Specification No. 578,709, have heretofore been prepared from dimethylterephthalate, which is trans-esterified with the appropriate diol, such as ethylene glycol, and then polycondensed to form the super polyester. Polyester preparation via dimethylterephthalate has been considered an essential step by reason of the exceptionally high purity requirements imposed on the polyester.

With the advent of improved processes for the manufacture of terephthalic acid, much attention has been directed to obtaining polyesters by direct esterification of terephthalic acid with the diol. This has mani-

fest advantages of simplicity and economy as compared with the dimethylterephthalate route. As yet, however, there remains serious difficulty in obtaining terephthalic acid of suitable purity. Unless the initial terephthalic acid is virtually completely free from extraneous contaminants, the polyester will have too low a melting point and will be of unsatisfactory colour.

It is believed that terephthalic acid impurities are of two types. First, the compound 4-carboxybenzaldehyde, an intermediate formed when terephthalic acid is obtained from the oxidation of paraxylene or other para disubstituted alkyl benzenes, is known to be deleterious with respect to polyester quality. Second, unidentified colour bodies, possibly of the benzyl or fluorone structure, are usually present as trace by-products of most terephthalic acid production processes, and yield off-colour polyesters. Any method of purifying terephthalic acid must reduce or eliminate both the 4-carboxybenzaldehyde (4-CBA) and the other impurities such as colour bodies.

In Patent No. 994,769 there is described and claimed a process for producing fibre-grade terephthalic acid from an impure terephthalic acid containing 4-carboxybenzaldehyde and other impurities, which process comprises catalytically hydrogenating said impure terephthalic acid in an aqueous solution at elevated temperature and pressure for a time sufficient to effect substantial reduction of said 4-carboxybenzaldehyde, and recovering a terephthalic acid of fibre-grade quality containing substantially less of said 4-carboxybenzaldehyde and other impurities.

It has now been found that polycarboxylic acid of a purity suitable for direct esterification with diols to produce films and fibres may be obtained from impure polycarboxylic aromatic acid containing

[Price 4s. 6d.]

BEST AVAILABLE COPY

aldehyde and other impurities by catalytically hydrogenating the aldehyde and other impurities in the impure acid by contacting a solution of the impure acid in demineralized water in the liquid phase at an elevated temperature and pressure and in the presence of hydrogen with a palladium-containing catalyst under mild hydrogenating conditions (as hereinafter defined) and recovering from the thus contacted solution purified acid containing substantially less aldehyde and other impurities. By this process, there is a chemical reduction of the aldehyde as well as a significant destruction of the colour body impurity. Surprisingly, when demineralised water is used in place of ordinary distilled water or steam condensate the useful life of the palladium-containing catalyst is increased markedly.

Thus according to the present invention a process for purifying aromatic polycarboxylic acid, which may be produced by liquid phase catalytic oxidation of polyalkyl aromatic hydrocarbons, to remove undesirable aldehyde and other impurities comprises contacting a solution of the impure acid in demineralised water in the liquid phase at an elevated temperature and pressure and in the presence of hydrogen with a palladium-containing catalyst under mild hydrogenation conditions, and recovering purified acid containing substantially less of said undesirable impurities. The process is particularly well suited for purification of aromatic dicarboxylic acids such as, for example, production of fibre-grade terephthalic acid from crude terephthalic acid. The recovering of purified acid is conveniently effected by crystallising the acid from the hydrogen treated aqueous solution. The palladium-containing catalyst suitably consists essentially of charcoal having supported thereon 0.05 to 1.0% by weight of palladium. Preferably the charcoal support is one having a surface area in the range of about 1,000 to 2,000 square meters per gram.

Crude aromatic polycarboxylic acid purified by the process of the invention may be obtained by catalytic liquid phase oxidation of a polyalkyl aromatic hydrocarbon with molecular oxygen in the presence of a heavy metal oxidation catalyst, said aromatic hydrocarbon having at least two nuclear alkyl hydrocarbon substituents whose carbon attached to the nuclear aromatic carbon has at least one hydrogen atom, and the crude aromatic polycarboxylic acid may have an aromatic polycarboxylic acid content of at least 99.0% by weight, preferably 99.5 weight percent, and may have as its principal impurity a carboxy aromatic aldehyde corresponding to said aromatic polycarboxylic acid. The hydrogenation step may be carried out by contacting the

solution of said crude acid in demineralised water in the liquid phase at a temperature in the range of about 450—600°F. and at a pressure sufficient to maintain a liquid phase and avoid precipitation of the acid in the presence of hydrogen with a palladium-containing hydrogenation catalyst for a time sufficient to effect substantial reduction of said aldehyde, and a purified acid containing less than 125 ppm of said aldehyde may be recovered.

According to a preferred embodiment of the present invention there is provided a method of producing fibre-grade terephthalic acid from crude terephthalic acid obtained by catalytic liquid phase oxidation of paraxylene with molecular oxygen in the presence of a heavy metal oxidation catalyst, which crude terephthalic acid has a terephthalic acid content of at least 99.0% by weight, preferably 99.5 wt. %, and which has as its principal impurity 4-carboxybenzaldehyde, which method comprises contacting a solution of said crude terephthalic acid in demineralised water substantially free of copper, in the liquid phase at a temperature in the range of about 450 to 600°F. and an elevated pressure sufficient to maintain a liquid phase in the presence of hydrogen with a palladium-charcoal hydrogenation catalyst for a time sufficient to effect substantial reduction of said aldehyde to para-toluic acid and recovering fiber-grade terephthalic acid by crystallization.

When terephthalic acid, or other aromatic dicarboxylic acid to be employed in super polyester production, is purified by the process of the present invention it is said to be of "fiber-grade" quality. The term "fiber-grade" does not denote a quantitative degree of purity, but rather describes a terephthalic acid which is sufficiently free from 4-carboxybenzaldehyde and other impurities so as to yield a super polyester upon direct esterification with a diol which is satisfactory for the intended purpose. Thus, terephthalic acid polyester intended for transparent film or white fiber will require significantly higher purity terephthalic acid than polyesters intended for tire reinforcing cord. The suitable 4-carboxybenzaldehyde (4-CBA) content of terephthalic acid for use in producing colorless film and fiber is less than about 125 parts per million (ppm) while for tire cord it may be as high as 500 parts per million or even higher. The p-toluic acid and 4-CBA contents of the fiber-grade terephthalic acid are each suitably less than 125 ppm, desirably less than 75 ppm, preferably less than 25 ppm, ideally essentially zero. The content of 4-CBA is more critical than p-toluic acid.

The process of the present invention has particular application to purification of

terephthalic acid produced by the liquid phase air (molecular oxygen) oxidation of paraxylene using a heavy metal and bromine as catalyst as described in British Patent Specification No. 807,091. The process of the present invention may also be used to advantage for purification of terephthalic acid from other processes for the catalytic liquid phase oxidation of para-dialkylbenzenes with molecular oxygen in the presence of heavy metal oxidation catalyst, such as those promoted with acetaldehyde or methyl ethyl ketone, for the terephthalic acids produced by these oxidation processes also contain 4-CBA impurity. Terephthalic acid from any source which contains 4-carboxybenzaldehyde and which is yellowish in color, can be converted to fiber grade terephthalic acid by the process of this invention.

The process of the invention is conducted at elevated temperature and pressure. By reason of its low solubility in water terephthalic acid requires either large volumes of water or high temperatures in order for the desired terephthalic acid production quantity to be put into solution. For reasons of economic equipment design and process operation, it is therefore desirable to conduct the process within the range of about 392 to about 700°F., although lower or higher temperatures may be used in particular circumstances. The most advantageous temperature range is about 450—600°F., e.g. 464—550°F. The quantity of water needed to dissolve the terephthalic acid at various temperatures may be estimated from the table below:

	<i>Terephthalic Acid</i> g./100 g. H_2O	<i>Temperature, °F.</i> for solution
40	1	365
	5	401
	10	468
	20	498
45	30	522

Ordinary process water is not completely satisfactory for use as the aqueous solvent in the process of the present invention, nor will ordinary distilled water do. It has been discovered that the palladium catalyst is poisoned by dissolved minerals, such as for example copper and other metals, therefore, it is critical to the useful life of the precious metal catalyst used to effect the particular hydrogenation of this invention that such minerals be removed from the water to be employed as solvent. Advantageously the water, conveniently steam condensate, is demineralized to a total dissolved solids content of less than 10 parts per million parts of water (ppm), preferably to less than 5 ppm, optimally to less than 1 ppm. The water may be demineralized

by any suitable process known to the art, such as for example by passing the water through a bed of chelating resin. The useful life of the palladium catalyst is greatly increased when minerals, and in particular copper, are removed. It is surprising that copper poisons the palladium since copper in various forms is known to be a hydrogenation catalyst.

Pressure conditions for the process of this invention depend upon the temperature at which this process is conducted. Since the temperatures at which significant amounts of the impure terephthalic acid may be dissolved in water are substantially above the normal boiling point of water, and since the hydrogenation section of the process of this invention is to be carried out with the solution in the liquid phase, the pressure will necessarily be substantially above atmospheric pressure.

It is preferred to trickle the liquid solution of acid through a bed of the catalyst because lower hydrogen partial pressure or hydrogen driving force is required than is required when the catalyst bed is operated liquid full. Either a static hydrogen atmosphere or a flow, concurrent or countercurrent, of hydrogen through the catalyst chamber may be maintained. Lower hydrogen partial pressures are required for the trickle or percolation method of conducting the hydrogenation section of the process of this invention because there is provided a thin film of the aqueous solution of the impure terephthalic acid on the catalyst particles and thus a lower hydrogen driving force is needed for the hydrogen to dissolve and diffuse through the thin liquid layer and reach the catalyst. For such percolation method of conducting the hydrogenation a continuous flow or atmosphere of hydrogen is not essential. However, for maximum hydrogenation rates it is beneficial to dissolve at least some hydrogen into the solution, conveniently in the acid dissolver, prior to contacting it with the catalyst. The process of this invention can be practiced by intermittent introduction of hydrogen into the bed of extended catalyst during the continuous introduction of the aqueous solution of impure terephthalic acid. The minimum of hydrogen to be introduced intermittently is, of course, an amount of hydrogen in excess of that required for reduction of the dissolved impurity so that adsorption of the excess hydrogen in the porous catalyst support can be simultaneously accomplished. Very little hydrogen is consumed by the purification process of this invention.

It is also advantageous in conducting the process of this invention, especially for the methods involving flow contact of the aqueous solution with hydrogen catalyst, to im-

pose on the aqueous solution being treated a pressure above the pressure required to maintain a liquid phase of the aqueous solution of impure terephthalic acid. This additional pressure will prevent premature crystallization of the acid due to minor process pressure variations causing vaporization of some of the solvent. This can be readily accomplished by use of an inert gas such as nitrogen. By "inert" gas is meant that gas which is not reactive with the terephthalic acid or the hydrogen or solvent. Nitrogen is a convenient inert gas. Also, the use of nitrogen permits the dilution of hydrogen to be introduced into the process of this invention and thereby provide low partial pressures of hydrogen to minimize over-hydrogenation such as, for example, saturation of aromatic nuclei.

In summary of the foregoing with respect to the hydrogenation section of the process of this invention, the hydrogen partial pressure employed in the preferred trickle system can vary in the range of from one atmosphere (14.7 psia) to 150 psi or more, preferably in the range of about 50 to 100 psi. It will be appreciated that the hydrogen driving force can be so great as to produce severe hydrogenation causing, for example, nuclear hydrogenation of the benzene ring of terephthalic acid, thereby converting some of the terephthalic acid to hexahydroterephthalic acid (cyclohexane-1,4-dicarboxylic acid), an undesirable impurity. Such severe hydrogenations should be avoided to prevent the inclusion of additional impurities to be removed in the crystallization section. Mild hydrogenation conditions should therefore be used. By the term mild hydrogenation conditions as used herein and in the appended claims, is meant hydrogenation conditions which effect hydrogenation of aldehyde functional groups but which do not effect significant hydrogenation of either carboxyl groups or aromatic nuclei.

Hydrogen treating time, or space velocity, will depend on the initial terephthalic acid purity, that is, the amount of impurity to be reduced, on the desired fiber-grade specifications imposed on the purified terephthalic acid, and on other conditions of the hydrogenation such as, for example, catalyst activity. Ordinarily, a treating time, i.e. contact time with the catalyst within the range of about 0.001 to about 10 hours, advantageously about 0.01 to 2 hours, will suffice for most operations. Although treating time is not a critical variable, it must be taken into consideration with regard to the aforementioned severe hydrogenation and its side effects.

Conditions for conducting the process of this invention can be readily ascertained, with respect to adequate vis-a-vis too severe

hydrogenation, by simple tests under the conditions selected to be employed with the particular method of conducting the process of this invention. For example, by conducting these simple bench-scale tests there can be readily determined contact time in a flow system and hydrogen driving force for a percolation-type flow system, which enhance the formation of p-toluic acid and avoid formation of cyclohexane-1,4-dicarboxylic acid to a point beyond which this side product is retained in the solvent under the conditions used for crystallizing purified terephthalic acid from the hydrogen treated solution.

The palladium hydrogenation catalyst for use in the inventive process must have sufficient hydrogenation activity to convert the aldehyde carbonyl group on the 4-carboxybenzaldehyde at least to a methylol group, e.g. p-methylol benzoic acid, and to destroy, or otherwise render innocuous, other impurities present in the feed terephthalic acid. Palladium supported on adsorbent charcoal in the amount of 0.05—1.0 weight percent Pd based on total catalyst is suitable as the hydrogenation catalyst. Advantageously, palladium contents in the range of about 0.1—0.5 weight percent may be used, with about 0.1—0.3 weight percent palladium being the preferred palladium content for use in trickle beds of catalyst. The higher palladium contents tend to produce over-hydrogenation while the lesser amounts suffer some loss in hydrogenation activity as compared with catalysts of the preferred palladium content.

The adsorbent charcoal support for the palladium may be any such support which has sufficient mechanical strength and surface area. It has been found that palladium-charcoal catalysts having a palladium content in the preferred range of 0.1—0.3 weight percent and also having a very high surface area in the range of about 1,000—3,000 square meters per gram of catalyst are particularly well suited for use in the present invention.

The hydrogen treated solution is preferably filtered to remove any suspended solids, such as catalyst support fines and extraneous materials, of about 5 microns and larger in size. The filter requirements are discussed below. The purified acid is then recovered from the filtered solution. Crystallization is a convenient method for recovering the acid. Either batch or continuous crystallization may be employed in the crystallization section, and preferred embodiments of continuous and batch systems are discussed below in conjunction with the Figures in the accompanying drawings. Crystallized acid is recovered by centrifuging during which further purification is effected by washing the centrifuge

cake. The crystals are dried in a rotary kiln to a moisture content below about 1 wt. %, preferably about 0.02—0.06 wt. %, to prevent caking during subsequent storage and shipping.

Regarding materials of construction, it is advantageous to use titanium and/or titanium clad steel for metallic surfaces exposed to TA-water solutions at temperatures above about 350°F. Below this temperature type 304 stainless steel is satisfactory except for the dryer tubes where type 316 stainless steel is preferred. Reinforced polyester is also suitable as an alternate material for use at temperatures below about 250°F.

It has been discovered that, surprisingly, titanium may be used for corrosion protection in contact with the acid solution, and protected from hydride formation and sloughing under reducing environment conditions in contact with hydrogen at temperatures above 350°F. and pressures above 750 psi by forming a blue oxide coating on the titanium. Such temperature and pressure conditions are encountered in the process of the present invention in such places as, for example, the dissolver preheater, dissolver, reactor, filters, crystallizers and piping. The oxide coating is conveniently formed and maintained as required, by including a small amount of oxygen, suitably as air, in the solvent-acid slurry feed to the dissolver preheater. Thus all titanium parts in contact with the corrosive solution under corrosion and reducing conditions will be protected.

Turning now to the drawings, Figure 1 is a simplified schematic flow plan of a preferred embodiment of the invention. Figures 2 and 3 are simplified schematic flow plans illustrating preferred embodiments of alternate continuous and batch crystallization systems, respectively. It is to be understood that these embodiments are for the purpose of illustration and are not to be regarded as a limitation of the scope of the present invention.

Referring now to Figure 1, dry crude terephthalic acid (TA), feed from source 10, such as for example a storage silo, is transferred via line 11 into crude terephthalic weigh hopper 12. Crude terephthalic acid is fed from the weigh hopper at a constant rate into the feed slurry tank 13 by the crude terephthalic feeder 14 which suitably can be any solids transfer feeder, such as, for example, a Star feeder. The crude terephthalic feeder 14 sets the nominal feed rate to the process, but since such devices are somewhat inaccurate, the average flow rate is determined by weight as measured by the terephthalic acid weigh hopper 12. Recycled demineralized water from line 16 is added to feed slurry tank 13 on flow

control to provide a slurry concentration of crude TA in water of approximately 15—30 weight percent, preferably about 20—25 wt. %, and in this example about 23 weight percent total solids. Slurry hold-up in feed slurry tank 13 of about 45 minutes at normal level is sufficient to dampen out fluctuations in the TA and water feed rates to the tank. The temperature in feed slurry tank 13 is maintained at a temperature in the range of about 100—300°F., preferably about 200°F. and the pressure is conveniently near atmospheric at temperatures below the boiling point of water by venting to the atmosphere. Feed slurry tank 13 is provided with an agitator to contact the solid crude TA and the recycled water in order to maintain a uniform slurry.

Slurry is withdrawn from feed slurry tank 13 via line 17 and transferred via high-pressure pump 18 via line 19 through preheater 21. Preheater 21 is conveniently a shell-and-tube heat exchanger with one tube pass. Normally the tube-side velocity of the slurry feed is not sufficient to keep the slurry in suspension, therefore it is advantageous to mount the heat exchanger vertically and employ downflow to prevent loss of effective tube surface as a result of settling of solids. Suitable preheater outlet conditions of temperature and pressure are about 530°F. and 985 psia, respectively. The preheated slurry is passed via line 22 into dissolver 23.

The reactor feed stream is passed upflow through the dissolver 23 which provides a residence time of approximately 20 minutes. The dissolver 23 is provided with an agitator to suspend the solids and to maintain the proper environment for a high solution rate of the crude TA into the water. A clear solution of TA in water overflows from the dissolver 23 via line 24 to the hydrogenation reactor 26 by gravity. This solution, when formed from a slurry of approximately 23 weight percent solids, contains about 30 pounds of crude TA per 100 pounds of water at 530°F. and 985 psia. The precipitation (crystallization) point for this solution is 520°F., therefore the solution at 530°F. is only about 10° hotter than the precipitation point.

Crude terephthalic acid solution from line 24 flows continuously into a distribution pan at the top vapor space of the hydrogenation reactor 26. Overflow from the pan trickles onto the palladium-on-carbon catalyst. Flow of hydrogen is advantageously co-current to flow of the TA solution through the catalyst bed, however, counter-current flow can be used. The bed is supported by a screen about equivalent to 8-gage Tyler mesh. Catalyst particles are of such size that about 95 weight percent are retained on this screen. However,

less than 5 percent of the catalyst is lost from the bed because of the filtering action of the bed itself. Space is provided within the reactor vessel 26 beneath the catalyst bed for vapor disengaging and liquid-level control. Effluent vapors are vented directly to the atmosphere from this vapor space via valved line 38, and liquid level control is maintained by throttling this vented stream.

Hydrogen from source 27, preferably in admixture with an inert gas such as nitrogen, is passed via line 28 into gas preheater-saturator 29. Demineralized water from source 31 is also passed via lines 32 and 33 into gas preheater-saturator 29 wherein the hydrogen-containing gas is heated to reaction temperature and is at least partially, preferably essentially completely, saturated with water vapor. Water-saturated gas from the preheater-saturator 29 is passed via lines 34 and 36 into the top vapor space of the reactor 26 and via lines 34 and 37 into the center section of the dissolver 23 so that hydrogen is dissolved in the solution and thus is readily available to effect hydrogenation upon contact with the catalyst in reactor 26.

Saturation of gas with water in preheater-saturator 29 is for the purpose of preventing localized crystallization of TA from the solution with consequent plugging which would occur if dry gas were fed into the reactor depriving the solution of water. The necessary degree of saturation of the hydrogen stream with water depends upon the equilibrium solubility of solid in the liquid, the inlet liquid temperature, and the amount of hydrogen which is consumed by the reaction. If pure hydrogen is used without inert diluent, the inlet gas stream is saturated at 530°F. and the reactor is pressure controlled, then the pressure of hydrogen in the reactor will be below 100 psia for liquid feed temperatures of 530°F. or above. The hydrogen partial pressure in the reactor will decrease to as low as 50 psia as the temperature is increased to 535°F. The hydrogen partial pressure is greater than 100 psia for liquid feed temperatures below 530°F. but there is a smaller quantity of vent gas due to steam condensation. At a reactor temperature of 525°F. and the normal hydrogen feed rate of 0.37 moles of hydrogen flowing through the reactor per 10,000 pounds of solution feed, the vent stream will decrease to about one-fourth of the saturated gas feed rate. The normal hydrogen partial pressure in the reactor is about 100 psi with the water vapor pressure contributing an additional 885 psia. If lower hydrogen partial pressures are used, it is advantageous to include an inert gas, such as nitrogen, with the hydrogen gas feed in order to provide a pressure pad to preclude vaporization of sol-

ent, and consequent precipitation and plugging due to minor process pressure variations.

Control of liquid stream temperature is critical to stable operation. Care must be taken that the stream does not contact local cold or hot spots in pipes or vessels. In particular, if the liquid stream temperature rises above about 540°F., boiling occurs with resulting sodification of TA. Experience has indicated that it is practically impossible to redissolve this material.

Hydrogenated solution is withdrawn from reactor 26 via line 39 and passed through reactor effluent filter 41 to remove any catalyst fines resulting from attrition of the carbon catalyst base. The filter elements are capable of removing particles of about 5 microns and larger in size. The filter elements have a minimum pressure drop corresponding to about 1 gpm/ft.²/psi, with a desired maximum total pressure drop of 10 psi. Filter elements are conveniently cleaned by flushing with hot water and, if necessary, by soaking in dilute caustic. This procedure will remove from the elements any precipitated TA deposited during depressuring of the filter prior to backwashing. Prior to putting a new or cleaned filter on stream it should be filled with water to prevent plugging due to TA solidification. Although only one filter is shown in Figure 1, it is contemplated that two or more filters may be used so that at least one filter may be in service while another is being cleaned.

Since the TA solution is highly corrosive at reactor effluent temperature, careful selection of suitable corrosion resistant elements for use in the filter is required. Filter elements from sintered titanium are satisfactory from the standpoint of corrosion, but their mechanical strength is borderline. Porous carbon beds of either loose carbon particles or bonded carbon particles have been found to be particularly suitable for this filtering application.

A suitable test to determine the effectiveness of the filter is to dissolve 5 grams of product TA in dimethylformamide and pass the resulting solution through filter paper to remove any solid fines. This filter paper is compared against a standard in which 0 represents clean filter paper and 5 is approximately gray in tone. Product TA having a rating of 0 to 1, barely distinguishable from clean filter paper, is considered satisfactory.

Filtered reactor effluent is passed via line 42 and inlet valve 82 to crystallization section 43 which is discussed in detail below and illustrated as alternate continuous and batch crystallization systems in Figures 2 and 3. In the crystallization section water is removed from the hot TA solution by

high rate evaporative cooling. As a result of both the cooling and the solvent removal, TA crystallizes from solution. Evaporated water is condensed and the condensate is withdrawn from the crystallization section and passed via line 44 into recycle solvent drum 46. The slurry of TA crystals resulting from the crystallization is withdrawn from the crystallization section via line 47 and passed into centrifuge feed tank 48 which is vented to the atmosphere by line 49. The centrifuge feed tank 48 is provided with an agitator to maintain the slurry of TA crystals in suspension. The TA slurry is passed from the centrifuge feed tank 48 via valved line 51 into one or more centrifuges 52 wherein the crystals are separated from the mother liquor and the crystals washed with fresh demineralized wash water obtained from source 31 via lines 32, 53 and 54. Wash water from the centrifuge is passed via line 55 into the recycle solvent drum 46. Mother liquor is withdrawn from the centrifuge and discarded via line 56. Purified TA crystals from the centrifuge 52 are withdrawn from the centrifuge and fed via auger feeders 57 and 57a into rotary kiln crystal dryer 58 which is heated by steam from source 59. Inert gas, such as nitrogen, from source 61 may be passed via line 62 into and through drying kiln 58 to assist in removing moisture from the TA crystals. The product is dried to a moisture content of about 0.05 wt. percent water. Inert gas and water vapor containing some TA fines are withdrawn from the kiln 58 and passed via line 63 into dryer-scrubber 64 wherein the gases are washed countercurrently by a stream of fresh demineralized water. The water is introduced to the dryer-scrubber 64 from source 31 via lines 32, 53 and 66 and descends counter-currently to the rising gas stream removing TA fines from the gases which are vented from the scrubber via line 67. Water containing TA fines is withdrawn from the dryer-scrubber 64 and passed via line 68, pump 69 and line 71 into the recycle solvent drum 46. The solvent drum is vented to the atmosphere via line 72. An agitator is provided within the solvent recycle drum 46 in order to maintain undissolved particles of TA, primarily from scrubber 64, in suspension. Recycle solvent water is withdrawn from the recycle solvent drum 46 and passed via line 73, pump 74 and line 16 into the feed slurry tank 13. Dried purified TA product is withdrawn from the drying kiln 58 and passed via conveyor 76 to storage.

The purified product contains less than 25 ppm by weight of 4-CBA and also less than 95 ppm by weight of p-toluic acid. The T.E.G. color of the product is below 50 which is well below the suitable maxi-

mum of 150 and the desirable maximum of 100.

The 4-carboxybenzaldehyde content was determined by dissolving the terephthalic acid in dilute alkali and buffering to a pH of 9, followed by polarographic analysis to determine "4-CBA" content. Color, expressed as "T.E.G. Color" (triethylene glycol color) was determined by esterifying 4.0 grams of the terephthalic acid with 28.4 cc of triethylene glycol at 500°F. followed by comparing the resultant solution color with American Public Health Association (APHA) standards.

Reference is now made to Figure 2 which is a simplified schematic flow plan illustrating a preferred embodiment of a continuous crystallization system for use in the process of the present invention. The first crystallizer 81 receives filtered reactor effluent at 530°F. and 985 psia via valved line 42 (Figure 1). Flashing occurs across the inlet valve 82 to 725 psia and a temperature of about 507°F. Vapor released during flashing is passed via valved line 83 and line 84 into the crystallizer condenser 86. The hold-up time in the first crystallizer 81 is about 1.1 hours. Approximately 30 percent of the dissolved terephthalic acid is precipitated at a rate of about 0.15 lbs. Tamin./100 lbs. H₂O. The first crystallizer 81 is provided with an agitator to suspend the terephthalic acid crystals in the form of a slurry. Slurry is withdrawn from the first crystallizer 81 and passed via valved line 87 into the second crystallizer 88. Slurry concentration in the effluent from the first crystallizer is approximately 7.1 weight percent solids.

The second crystallizer 88 is operated at 115 psia and a temperature of about 338°F. Vapor resulting from the further flashing of solvent in the second crystallizer 88 is passed via valved line 89 and line 84 into the crystallizer condenser 86. Hold-up time in the second crystallizer 88 is about 1.2 hours. The terephthalic acid crystallization rate in the second crystallizer is about 0.4 lbs. TA/min./100 lbs. H₂O. Effluent slurry concentration from the second crystallizer is approximately 29.1 weight percent solids. The second crystallizer 88 is also provided with an agitator to maintain the TA crystals in slurry suspension.

Slurry is withdrawn from the second crystallizer 88 and passed via valved line 91 into the third crystallizer 92 which operates at a temperature of about 228°F. and 20 psia with a liquid hold-up time of about 1.1 hours. Nearly all of the terephthalic acid, about 98.6 weight percent, is crystallized under the operating conditions in the third crystallizer. Flashed solvent vapors are withdrawn from the third crystallizer 92 and passed via valved line 93 and line 84

into the crystallizer condenser 86. The third crystallizer 92 is also provided with an agitator to maintain the crystallized TA in suspension in the form of a slurry. Condensate from crystallizer condenser 86 is passed via line 44 into recycle solvent drum 46 (Figure 1). Slurry containing about 32.5 weight percent solids is withdrawn from the third crystallizer 92 and passed via valved line 47 into centrifuge feed tank 48 (Figure 1).

In reference to Figure 3 which is a simplified schematic flow plan illustrating a preferred embodiment of a batch crystallization system, it is pointed out that this batch system and the previously discussed continuous crystallization system are alternative crystallization sections for use in the process of this invention as illustrated in Figure 1. Referring now to Figure 3, effluent hold tank 101 receives filtered reactor effluent continuously via valved line 42 (Figure 1) under temperature and pressure conditions of 530°F. and 985 psia, respectively. A small amount of solvent flashing occurs across the inlet valve 82 to about 885 psia with only a minor decrease in stream temperature. Essentially all of the dissolved hydrogen is released from the liquid in this vessel. Solvent vapor and gas is passed via valved line 102 and line 84 into crystallizer condenser 86.

While three crystallizer vessels are illustrated in Figure 3, it should be understood that any number, one or more, of crystallizer vessels may be employed. Hot TA solution is alternatively passed from effluent hold tank 101 into each of the crystallizers A, B and C via line 103 and valved manifold line 104. High pressure steam, nominally 1,000 psi, is used to pressure each crystallizer prior to its fill cycle in order to prevent flashing of the hot solution into a nearly empty crystallizer vessel causing plugging of the inlet line. This steam is introduced from source 106 via line 107 and valved manifold 108 into the vapor space of each crystallizer prior to its fill cycle. High pressure steam is also fed via valved line 109 into effluent hold tank 101 during its dumping cycle to displace charged solution therefrom preventing excessive solvent vaporization. This steam is then vented via valved line 102 and line 84 into the crystallizer condenser 86 during the hold tank's filling cycle.

The crystallization cycle of each crystallizer includes the following: vessel heating and pressurization with steam, filling, cooling and crystallizing, and dumping. The cooling period is divided into three regions of limiting condition:

- 1.) Crystallization rate,
- 2.) Vaporization rate, and
- 3.) Vapor loading and defoaming rate.

The rate of cooling during the first 15 minutes of the cooling and crystallization period is limited to a crystallization rate of 1.5 lbs. TA/100 lbs. H₂O/min. by controlling the rate of water vapor flow from the crystallizer. The final cooling period is self limited by the rate of release of water vapor from the liquid surface at the lower temperatures existing at the time. The maximum crystallization rate has been set at 1.5 lbs. TA/100 lbs. H₂O/min. in order to prevent shock cooling with the consequent formation of an excessive number of infinitesimal crystals and, more importantly, to prevent inclusion within the TA crystals of paratoluic acid and other impurities, which inclusion has been found to occur excessively at crystallization rates such as result when the solvent (water) vapor is flashed without controlling the evaporation rate such as can be conveniently done by throttling the vapor outlet line.

Crystallizer agitators are provided in each of the crystallizer vessels to maintain slurry suspension during the cooling and dumping cycles. Vapors from each of the crystallizers are passed via manifold line 110 and line 84 into crystallizer condenser 86.

Crystallizer effluent is transferred via manifold line 111 into the crystallizer hold tank 112 by pressuring the crystallizers with 150 psig steam from a source not shown. This transfer is performed under steam pressure to avoid flashing in manifold line 111 with consequent plugging. The effluent is flashed across the inlet valve 113 to atmospheric pressure in crystallizer hold tank 112, which pressure is maintained by venting to the atmosphere via valved line 114. Crystallizer hold tank 112 is provided with an agitator to maintain the TA crystals in slurry suspension. Slurry is pumped from the crystallizer hold tank 112 via line 116, transfer pump 117 and valved line 47 into centrifuge feed tank 48 (Figure 1).

Vapor loading and defoaming rate are handled according to conventional design techniques.

It is to be understood that the following Examples are for the purpose of illustration and comparison only and are not to be regarded as a limitation of the present invention.

EXAMPLE I

Fiber-grade terephthalic acid (TA) was produced from crude terephthalic acid containing 4-carboxybenzaldehyde (4-CBA) according to the process of the present invention as illustrated in Figure 1, employing distilled water as the solvent and 0.24 wt. per cent palladium on charcoal having a surface area of 1,800 square meters per gram as the hydrogenation catalyst. The distilled water was prepared and stored in

conventional equipment. Catalyst life was 350-400 lbs. of TA per lb. of catalyst before the 4-CBA content exceeded 50 ppm by weight.

- 5 The test was then repeated under essentially the same conditions except that the distilled water was deionized (demineralized) with a chelating resin prior to use as solvent. Catalyst life of a fresh sample of
10 the same catalyst and under essentially the same conditions as above was over 800 lbs. TA/lb. of catalyst without exceeding 50 ppm by weight of 4-CBA in the product. Thus, use of demineralized water as sol-
15 vent resulted in more than doubling the catalyst life as compared with the use of ordinary distilled water.

EXAMPLE II

- 20 In order to determine whether copper is a poison to the palladium-charcoal catalyst as used in the process of the present invention, 1 gram of TA containing less than 10 ppm of 4-CBA, 0.4106 gram of Pd on charcoal catalyst, 0.0131 gram of cupric acetate and 350 ml of deionized distilled
25 water were charged to a rocker bomb and the bomb pressured to 100 psig with hydrogen. The bomb and its content were heated to 470°F. and held at that temperature for 4 hours. The bomb was cooled, de-
30 pressed and 30 grams of TA containing 0.95 wt. per cent 4-CBA were added to the bomb contents, the bomb pressured to 200 psig with hydrogen and the bomb and contents
35 heated to 475°F. and held at that temperature for 2 hours, then cooled and de-
40 pressed. The recovered TA analyzed 1040 ppm 4-CBA. This 4-CBA content compared with the results of tests conducted as above but without addition of cupric acetate wherefrom the recovered TA contains
45 only 33 ppm of 4-CBA, demonstrates that copper will poison the palladium-charcoal catalyst.

- 45 In our copending Patent Application No. 21654/66 (Serial No. 1,152,575) there is described and claimed a process for purifying an aromatic polycarboxylic acid containing undesirable aldehyde and other im-
50 purities, which process comprises contacting a solution of the impure acid in water in the liquid phase at an elevated temperature and pressure and in the presence of hydrogen with a platinum group metal-
55 containing catalyst under mild hydrogenation conditions (as defined therein) and recovering from the resulting solution purified acid containing substantially less of said unde-
60 sirable impurities by crystallization employing controlled-rate evaporation cooling.

Further in our copending Patent Application No. 21655/66 (Serial No. 1,152,576) there is described and claimed a process for purifying an aromatic polycarboxylic acid

containing undesirable aldehyde and other 65 impurities, which process comprises contacting a solution of the impure acid in water in the liquid phase at an elevated temperature and pressure and in the pre-
70 sence of pre-humidified hydrogen gas with a platinum group metal-containing catalyst under mild hydrogenation conditions (as defined therein) and recovering purified acid containing substantially less of said unde-
75 sirable impurities.

WHAT WE CLAIM IS:—

1. A process for purifying an aromatic polycarboxylic acid containing undesirable aldehyde and other impurities comprising 80 contacting a solution of the impure acid in demineralised water in the liquid phase at an elevated temperature and pressure and in the presence of hydrogen with a pal-
85 ladium-containing catalyst under mild hydrogenation conditions (as hereinbefore defined) and recovering purified acid containing substantially less of said undesirable impurities.

2. A process according to claim 1, wherein the aromatic polycarboxylic acid is produced by liquid phase catalytic oxida- 90 tion of a polyalkyl aromatic hydrocarbon.

3. A process according to claim 1 or 2, wherein said recovering of purified acid is effected by crystallising said acid from 95 said solution.

4. A process according to claim 1, 2 or 3, wherein said palladium-containing catalyst consists essentially of charcoal hav- 100 ing supported thereon 0.05 to 1.0% by weight of palladium.

5. A process according to claim 4, wherein said charcoal has a surface area in the range of about 1,000 to 2,000 square 105 metres per gram.

6. A process according to any one of the preceding claims wherein the aromatic polycarboxylic acid is obtained by catalytic liquid phase oxidation of a polyalkyl aromatic hydrocarbon having at least two nuclear alkyl hydrocarbon substituents with the carbon attached to the nuclear aromatic carbon having at least one hydrogen atom, with molecular oxygen in the presence of a heavy metal oxidation catalyst, has an 115 aromatic polycarboxylic acid content of at least 99.0% by weight and has as its principal impurity a carboxy aromatic aldehyde corresponding to said aromatic polycarboxylic acid. 120

7. A process according to claim 6, wherein said solution is contacted in the liquid phase at a temperature in the range of about 450-600°F. in the presence of hydrogen with a palladium-containing hy- 125 drogenation catalyst for a time sufficient to effect substantial reduction of said aldehyde and purified acid is recovered containing less than 125 ppm of said aldehyde.

8. A process according to any one of the preceding claims, wherein the aromatic polycarboxylic acid is a dicarboxylic acid produced by catalytic liquid phase oxidation of a dialkyl aromatic hydrocarbon with molecular oxygen.
9. A process according to claim 8, wherein said acid is terephthalic acid, said dialkyl aromatic hydrocarbon is paraxylene, and said aldehyde is 4-carboxybenzaldehyde.
10. A process for the purification of an aromatic polycarboxylic acid substantially as hereinbefore described and exemplified by Example I.
11. An aromatic polycarboxylic acid when purified by a process according to any one of the preceding claims.
12. Terephthalic acid when purified by a process according to any one of claims 1 to 10.

MATHYS & SQUIRE,
Chartered Patent Agents,
Staple House,
51/52 Chancery Lane,
London, W.C.2,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1969.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

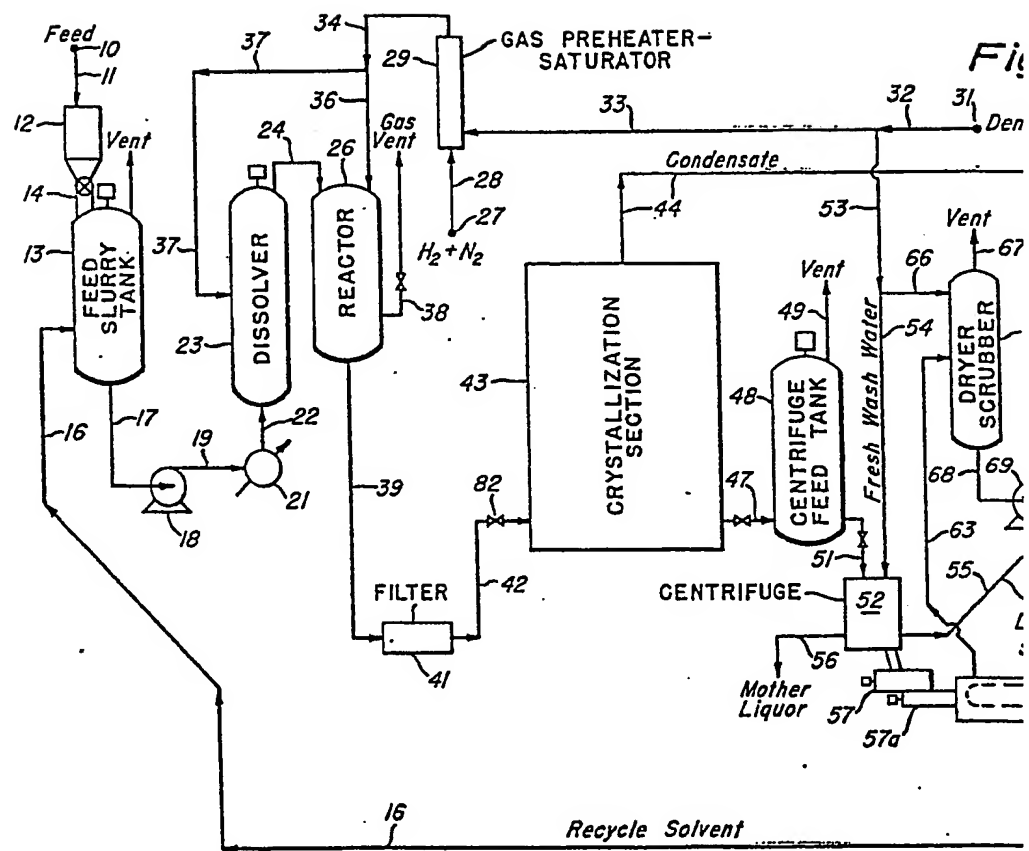
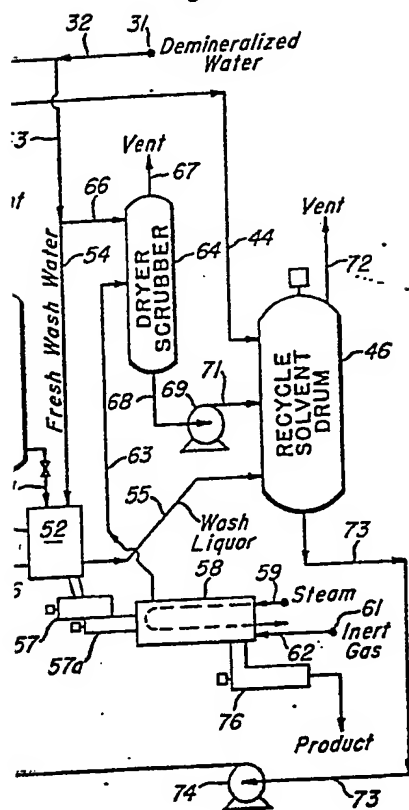
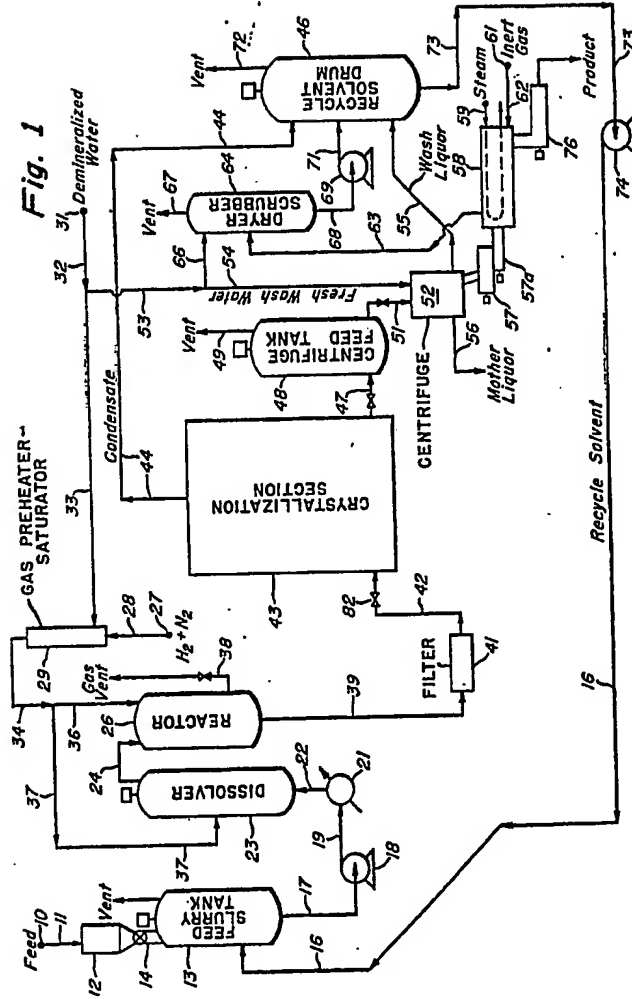


Fig. 1





CONTINUOUS CRYSTALLIZATION SECTION

BATCH CRYSTALLIZATION SECTION

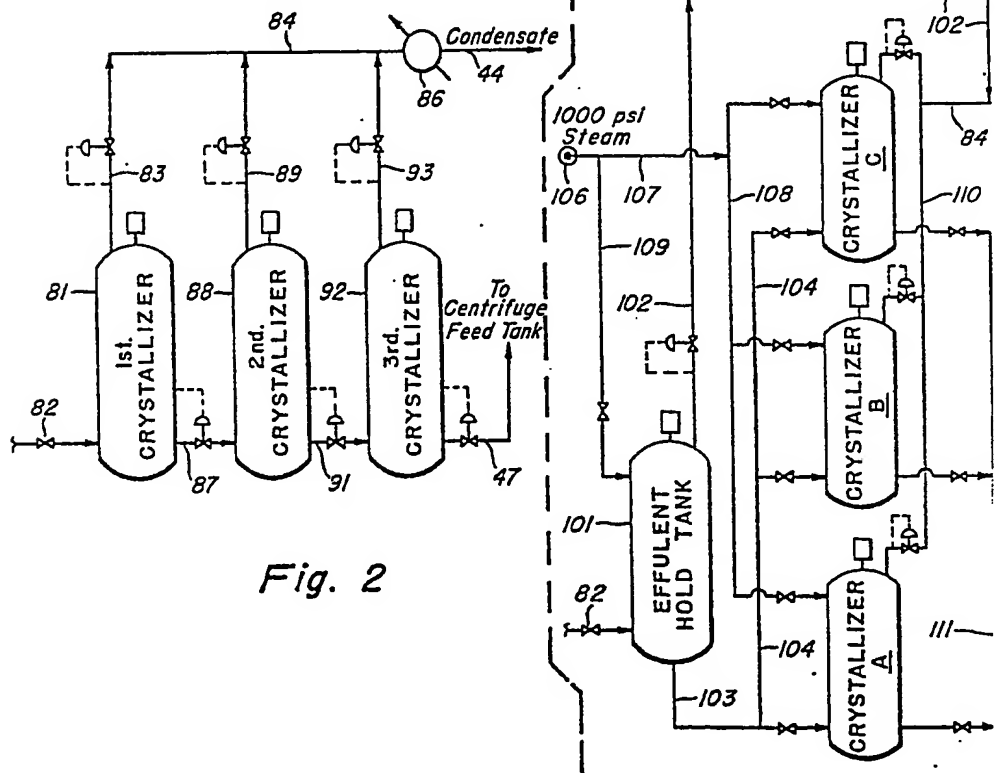


Fig. 2

STALLIZATION SECTION

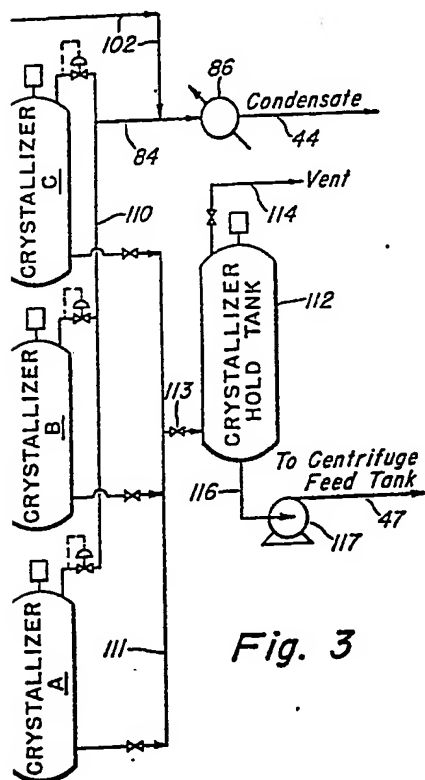


Fig. 3

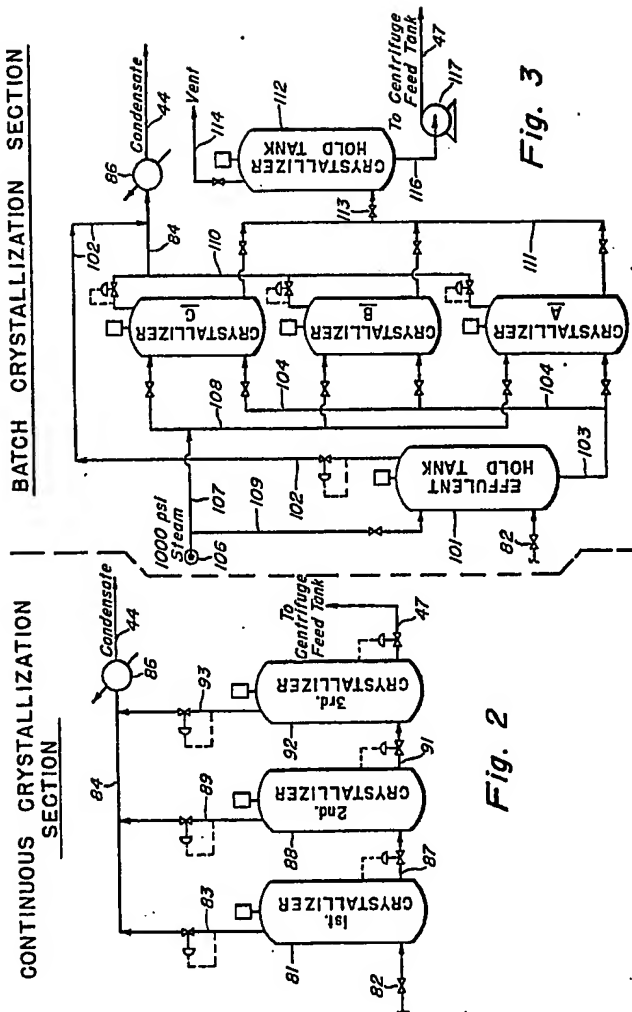


Fig. 2

Fig. 3